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Microbial contact enhances bioleaching of rare earth elements

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ABSTRACT

The mobility of rare earth elements (REEs) in monazite depends on microbial activity, attachment of bacteria on the mineral surface, phase association of the REEs, and which physiochemical and biological processes these phases are subjected to. To better understand the role of the phosphate solubilising bacterium, *Enterobacter aerogenes*, in REEs leaching, a series of monazite dissolution experiments was performed. The contact of bacteria with monazite was demonstrated to be advantageous for REEs bioleaching even though the same types of organic acids with similar concentrations were present during non-contact leaching. Monazite dissolution was observed to decrease in the following order: Biotic contact ≫ Biotic non-contact ≫ Spent media ≈ Abiotic at 30 °C. The attachment of bacteria on monazite surface by a co-localised atomic force microscopy (AFM) and confocal Raman microscopy (CRM) indicated no preferential attachment of bacteria to specific site on the monazite surface.

1. Introduction

In the last decade, rare earth elements (REEs), have been considered as “critical and strategic metals”, due to China's monopoly position and increased global demand in green technologies. Although REEs are relatively abundant in the Earth's crust, they are not evenly distributed around the world, and are mainly produced and processed in China (Ganguli and Cook, 2018; Zepf, 2013). Consequently, the prediction of exhaustible resources such as REEs is of profound significance, in that it not only aids governments to establish long-term resource plans but also contributes to maintain sustainable social and economic development (Wang et al., 2015). Considering the constant development of REEs industries, the Generalized Weng model, a widely used quantitative model in exhaustible resource forecast has been adopted to predict the production of the three major REEs in China (i.e., mixed rare earth, bastnasite and ion-absorbed rare earth) (Wang et al., 2015). The results suggested that countries with REEs resources should commence or continue their production to gradually decline dependency on China's supply (Wang et al., 2015).

Apart from the geopolitical challenges in REEs production, environmental issues can be a major concern as the extraction of REEs from their ores requires significant processing (Goodenough et al., 2018). The current conventional REE production, relies on high temperatures and harsh chemical treatments, has high energy consumption, and generates large volumes of toxic waste containing thorium, uranium, hydrogen fluoride, and acidic waste water (Hurst, 2010). Furthermore, as REEs-bearing ores may contain up to 10% thorium and uranium (Ragheb, 2011), emission of radioactive waste associated with REEs mining and extraction results in either contamination of the final REEs concentrate or the requirement for complicated disposal protocols (Ault et al., 2015). It has been reported that the environmental life cycle impacts of REEs production during chemical leaching are far greater than those for other metals (Vahidi and Zhao, 2016). Consequently, due to environmental restrictions, sustainable mining and production are now encouraged. Biotechnological mineral processing approaches have been developed as a sustainable alternative to chemical leaching of ores and waste streams. Biohydrometallurgy utilises microorganisms to generate bio-lixiviants which accelerate the dissolution of elements from their ores or other materials (Watling, 2016). Bioleaching processes are generally operated at relatively low temperature and atmospheric pressure, which reduces energy cost and gas emissions, and without relying on expensive and aggressive reagents (Bryan et al.,

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2015).

Despite the significant contribution of bioleaching to the extraction of base metals from sulfide minerals, very few studies have explored the application of microbes, in particular phosphate solubilising microorganisms (PSMs), to monazite and other phosphate minerals hosting REEs. Brisson et al. (2016) demonstrated the bioleaching of REEs (3–5% recovery) from monazite sand as the sole phosphate source by three phosphate solubilising fungi. In another study, Shin et al. (2015) examined the feasibility of using phosphate solubilising bacteria (PSB) for the bioleaching of REEs from monazite-bearing ore with maximum leaching yield for cerium (up to 0.13%).

The previous studies on REE bioleaching have focused on efficiency (Brisson et al., 2016; Hassanien et al., 2013; Shin et al., 2015) whereas little is known of the mechanisms involved and benefits of REEs dissolution to the microbes. Adhesion and colonization of the mineral surface are survival mechanisms for bacteria with nutrients in aqueous environments more accessible at surfaces (Busscher and van der Mei, 2012). Many studies on sulfide minerals demonstrate that microbial attachment and biofilm formation can stimulate pyrite bioleaching (Sand and Gehrke, 2006). Corbett et al. (2017) demonstrated that *Enterobacter aerogenes* leached 43% of the phosphate from tricalcium phosphate ($Ca_3(PO_4)_2$ or TCP) after 192 h, and of 12 known PSB released the greatest amount of REE from a monazite. Therefore, in this study, the mechanisms of bioleaching REE from monazite were systematically investigated with *E. aerogenes*. The study was designed to allow the bacteria to either be in contact with the monazite surface or to prevent contact between the bacteria and the mineral enabling us to investigate microbial bio-mobilization mechanisms involved in REE dissolution in terms of the importance of microbial colonization of mineral surfaces. Data from the monazite dissolution was used to develop a conceptual model to integrate the main phenomena affecting REE leaching. The results from this study will facilitate the development of sustainable bio-mining approaches REE extraction.

2. Material and methods

2.1. Monazite ore

The high grade weathered yellowish monazite ore was collected from the Mount Weld Mine (Lynas Corporation), and is hereafter referred to as MWM (Mt. Weld Monazite). Sample preparation and composition analysis were described elsewhere (Corbett et al., 2017). The total surface are of the MWM was 24,000 $cm^2\,g^{-1}$ as determined by Brunauer–Emmett–Teller (BET) analysis at CSIRO Minerals, Waterford, Western Australia. The BET surface area ($cm^2\,g^{-1}$) was analysed by the N_2 adsorption method at the temperature of liquid nitrogen (−196 °C) in a Micromeritics Gemini III 2375 (USA). Prior to the nitrogen adsorption measurements, each sample (approximately 0.6 g in weight) was degassed at 150 °C for 3 h in vacuum. The BET surface area was determined by using the N_2 adsorption data at 5 different standard pressures (0.05, 0.15, 0.2, 0.25 and 0.3) at −196 °C. Any results were rejected and the samples re-tested if the correlation coefficient of a plot of the 'BET Function' through the 5 points was lower than 0.9997. Before bioleaching experiments, the mineral samples were sterilized by gamma irradiation at 50 kGy for 11 h (ChemCentre, Bentley, Western Australia).

2.2. Bioleaching experiment

Enterobacter aerogenes (ATCC® 13,048™) was grown to exponential phase at 30 °C in National Botanical Research Institute Phosphate (NBRIP) medium (Nautiyal, 1999), with shaking at 140 rpm, and harvested by centrifugation (3600*g*, 10 min). Cells were resuspended in sterile Tris-HCl buffer (100 mM, pH 7.2), centrifuged (3600 *g*, 5 min) and washed twice more to remove any trace of phosphate. The ability of *E. aerogenes* to bioleach MWM as a phosphate source, was evaluated in 500 mL Erlenmeyer flasks. Bioleaching was carried out over 18 days at 30 °C in triplicate, at 120 rpm in an orbital shaking incubator (RATEK, Model No: OM11)in 200 mL of modified NBRIP media (3% w/v glucose and pH 7.00 ± 0.25), with 0.5% v/v bacterial inoculum (initial density 1×10^7 cells mL^{-1}) and 1% pulp density of sterilized monazite. Cell-free abiotic controls were carried out under the same conditions. Bioleaching was monitored by measuring the soluble concentration of Ce, La, Pr, Nd, Fe, P, Th, U, and Y in the leachate.

Non-contact experiments were conducted in similar conditions to those described above. Snakeskin® dialysis tubing (10 K MWCO, 35 mm, ThermoFisher SCIENTIFIC, catalogue number 88245) with Snakeskin™ Dialysis Clips (ThermoFisher SCIENTIFIC, catalogue number 68011) were used to study the possible mechanisms for leaching REE from monazite as follows:

1. For biotic contact leaching of monazite, dialysis bag, 200 mL media, and 1 mL of bacterial suspension were placed in 500 mL Erlenmeyer flasks. The monazite in this experiment was not sealed in the dialysis bag, so that bacteria were free to colonize monazite surfaces.
2. For abiotic contact leaching monazite and media were placed in 500 mL Erlenmeyer flasks.
3. For biotic non-contact leaching the monazite was sealed in the dialysis bag. This sealed dialysis bag, media, and 1 mL of bacterial culture were placed in Erlenmeyer flasks.
4. For abiotic non-contact leaching monazite was sealed in dialysis bag. This sealed dialysis bag and media were placed in Erlenmeyer flasks.

The pore size of the dialysis bag is sufficiently small to prevent bacterial migration through the bag, but large enough to allow the homogenous transfer of nutrients for bacterial growth.

Molar dissolution rates (r) per surface area of the ore and time ($mol\,cm^{-2}\,s^{-1}$) were calculated as using Eq. (1):

$$r = \frac{r_{volumetric}}{c_{solids} \times M \times A} \quad (1)$$

where $r_{volumetric}$ refers to the volumetric leaching rate ($g\,L^{-1}\,s^{-1}$) obtained from the slope of the soluble element concentration versus time plot, c_{solids} represents the initial solid concentration in the flasks ($10\,g\,L^{-1}$), M is molar mass of the element (140.1, 138.9, and 88.9 $g\,mol^{-1}$ for Ce, La, and Y, respectively), and A is the total mineral surface area ($cm^2\,g^{-1}$) obtained with BET.

2.3. Leaching of MWM with spent media

Pregnant solutions were prepared as described in Section 2.2. After 24 h incubation and pH decrease (pH = 3.4), the media was aseptically filtered (0.20 μm, Satorius). One gram of MWM was added to 50 mL of the filtered spent medium in 200 mL flask and incubated at 30 °C with shaking at 120 rpm for six days. Leaching was monitored by measuring the soluble concentration of Ce, La, Pr, Nd, Fe, P, Th, U, and Y in the leachate.

2.4. Analytical methods

Samples were taken at 0, 2, 3, 6, 9, 12, 18 d and pH measured using a pH meter (Ionode IJ series pH probe). Thereafter, samples were filtered (0.20 μm, Satorius) and assayed for REEs, Y, Th and U concentrations by ICP-MS (Agilent Technologies 7700 series, Bureau Veritas Australia Pty Ltd., Canning Vale, Western Australia) and the average values were reported. Organic acids were identified by high performance liquid chromatography (HPLC) (Agilent 1200, Curtin Water Quality Research Centre, Bentley, Western Australia) coupled with a diode array detector (DAD, Agilent). Injection volume was set as 50 μL for the samples. Compound separation was achieved with a C18 reverse phase column (Agilent, 5 μm, 4.6 × 250 mm). The isocratic